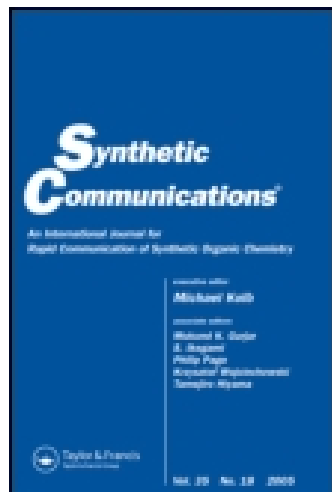


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Metal-Free Direct Hydrosulfonylation of Azodicarboxylates with Sulfinic Acids Leading to Sulfonylhydrazine Derivatives

Jiangwei Wen^a, Wei Wei^a, Daoshan Yang^a, Yufeng Fan^a, Lulu Fu^a & Hua Wang^a

^a Key Laboratory of Life Organic Analysis and Key Laboratory of Pharmaceutical Intermediates and Analysis of Natural Medicine, School of Chemistry and Chemical Engineering, Qufu Normal University, Qufu, Shandong, China

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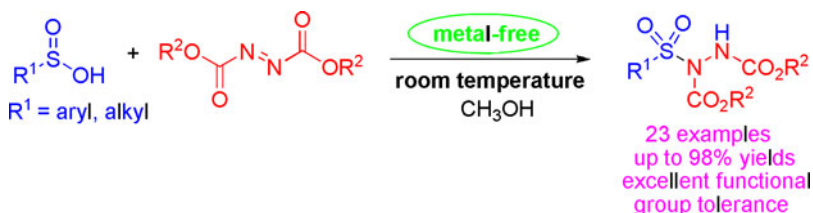
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METAL-FREE DIRECT HYDROSULFONYLATION OF AZODICARBOXYLATES WITH SULFINIC ACIDS LEADING TO SULFONYLHYDRAZINE DERIVATIVES

Jiangwei Wen, Wei Wei, Daoshan Yang, Yufeng Fan, Lulu Fu, and Hua Wang

Key Laboratory of Life Organic Analysis and Key Laboratory of Pharmaceutical Intermediates and Analysis of Natural Medicine, School of Chemistry and Chemical Engineering, Qufu Normal University, Qufu, Shandong, China

GRAPHICAL ABSTRACT



Abstract A metal-free direct hydrosulfonylation protocol of azodicarboxylates with sulfinic acids has been developed for the construction of sulfonylhydrazine-1,2-dicarboxylates at room temperature. This methodology provides an efficient and practical approach to prepare various sulfonylhydrazine-1,2-dicarboxylates in good to excellent yields, which has the advantages of operation simplicity, environmental friendliness, high atom economy, and mild reaction conditions.

Keywords Hydrosulfonylation; metal-free; sulfinic acids; sulfonylhydrazine-1,2-dicarboxylates

INTRODUCTION

As extremely valuable organic compounds, sulfonylhydrazines and their derivatives have attracted considerable attention both from synthetic and medicinal chemists, because they not only serve as useful synthetic precursors for a variety of

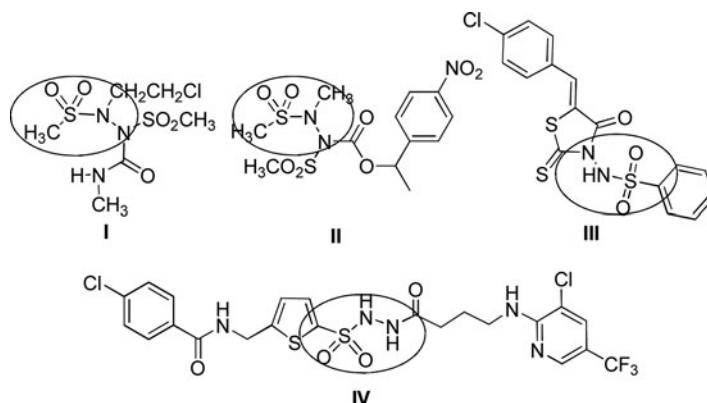
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Address correspondence to Wei Wei or Hua Wang, Key Laboratory of Life Organic Analysis and Key Laboratory of Pharmaceutical Intermediates and Analysis of Natural Medicine, School of Chemistry and Chemical Engineering, Qufu Normal University, Qufu 273165, Shandong, China. E-mail: weiweiqfnu@163.com; huawang_qfnu@126.com

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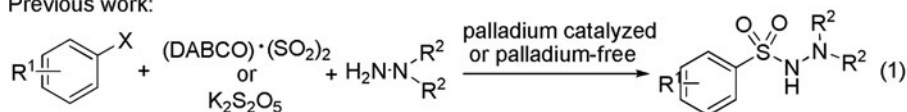
organic transformations^[1] but also are an important class of pharmaceutical molecules with a broad spectrum of biological activities.^[2–6] For example, as shown in Scheme 1, compound **I** (VNP40101 M or laromustine)^[3] is a sulfonylhydrazine alkylating agent that has been demonstrated to have antitumor activity in preclinical studies; compound **II** (KS900)^[4] is a alkylating agent that targets the *O*-6 position of guanine in DNA; compound **III**^[5] exhibits potent inhibitory activity of HCV RNA polymerase (NS5b); and compound **IV**^[6] can be used as a selective inhibitor of *c*-Jun *N*-terminal kinases (JNK). In addition, sulfonylhydrazines derivatives can also be used in the production of azo dyestuffs^[7] or as blowing agents in cellular rubber and plastics.^[8] Generally, sulfonylhydrazine compounds are prepared by the amination of sulfonyl chlorides with the corresponding hydrazines, which usually suffer from poor tolerance of functional groups and the generation of large amounts of unwanted by-products. Recently, palladium-catalyzed or palladium-free aminosulfonylation reactions of aryl halides, boronic acids, and diazonium salts leading to sulfonylhydrazines have been proposed by Nguyen et al.^[9] and Ye and Wu,^[10] in which the use of DABCO·(SO₂)₂ or K₂S₂O₅ as the sulfonylation reagent was thought to be a breakthrough [Scheme 2, Eq. (1)]. In 2014, Wang et al. also reported a copper-catalyzed, three-component reaction of triethoxysilanes, sulfur dioxide, and hydrazines for the construction of sulfonylhydrazines [Scheme 2, Eq. (2)].^[11] Despite some advantages of these reactions, they might in a way encounter low atom-economy or the use of transition-metal catalyst.^[9,10a,b,11] Thus, the development of more simple, convenient, atom-economical, and green methods for the construction of sulfonylhydrazine compounds is still highly desirable.

Very recently, sulfinic acids as a simple and readily available sulfonylating source have been emerged for constructing sulfone-containing compounds with high atom efficiency.^[12,13] Here, we report a simple, highly efficient, and catalyst-free direct hydrosulfonylation of azodicarboxylates with sulfinic acids leading to sulfonylhydrazine-1,2-dicarboxylates via S-N bond formation at room temperature with 100% atom efficiency [Scheme 2, Eq. (3)].

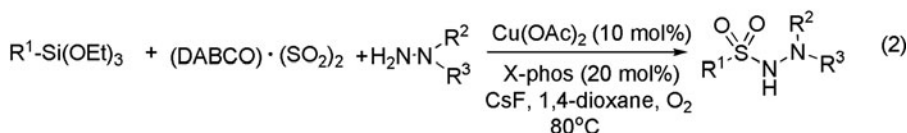


Scheme 1. Examples of bioactive sulfonylhydrazine compounds.

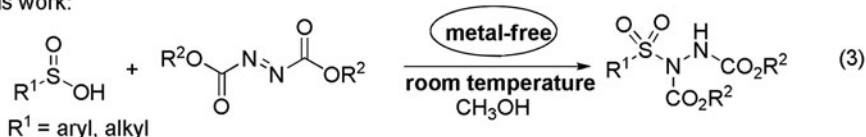
Previous work:



X = I, Br, B(OH)₂, N₂BF₄



This work:

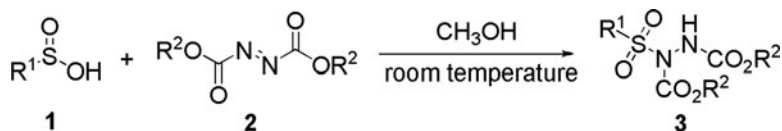


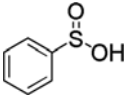
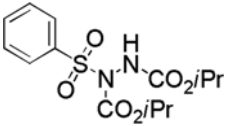
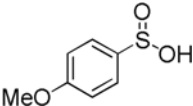
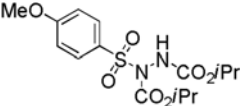
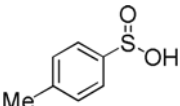
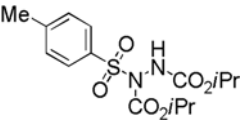
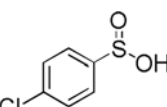
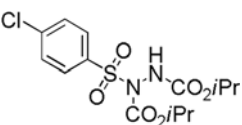
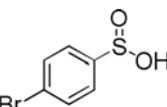
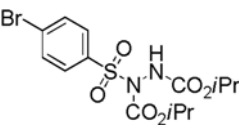
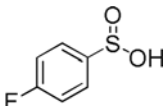
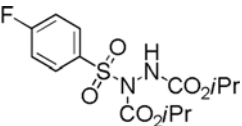
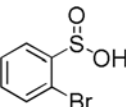
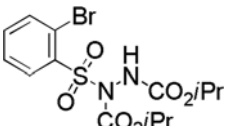
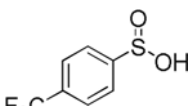
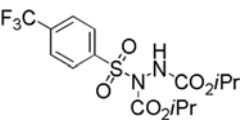
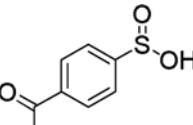
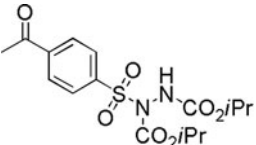
Scheme 2. Methods for synthesis of sulfonylhydrazine compounds.

RESULTS AND DISCUSSION

Initially, the reaction of benzenesulfonic acid **1a** with diisopropyl azodicarboxylate **2a** catalyzed by Cu(OAc)₂ was investigated. To our delight, the desired product was obtained in 81% yield in tetrahydrofuran (THF) at room temperature (Table 1, entry 1). Further optimization of catalysts showed that the similar yields were achieved in the presence of Pd(OAc)₂ and AgNO₃ (Table 1, entries 2 and 3). Based on the findings, we envisioned that the efficiency of this reaction might not be affected by the metal salts. As expected, the desired product was obtained in 86% yield when the reaction was performed in the absence of catalyst (Table 1, entry 4). Moreover, the increase of temperature did not improve the efficiency of the reaction (Table 1, entries 5 and 6). The relatively lower yields were obtained when bases such as Et₃N, pyridine, and 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU) were employed as the additives (Table 1, entries 7–9). The experimental results indicate that the reaction efficiency could be significantly influenced by the employed solvents (Table 1, entries 4 and 10–16). Among the various solvents tested, protic solvent CH₃OH was proven to be the optimal reaction medium compared to the others (Table 1, entry 12). Notably, the desired product could also be obtained in good yield (92%) when CH₃OH/H₂O was used as cosolvent (Table 1, entry 18).

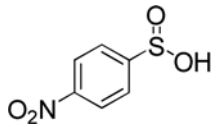
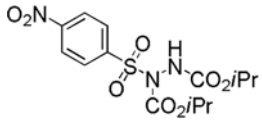
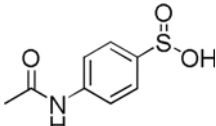
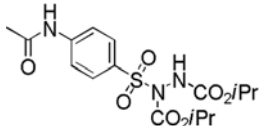
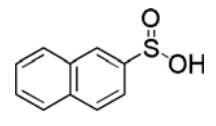
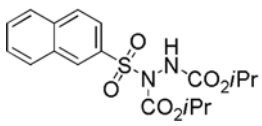
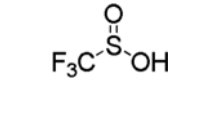
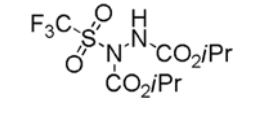
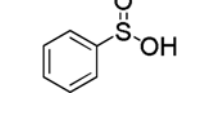
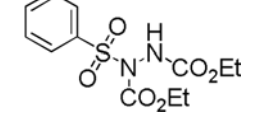
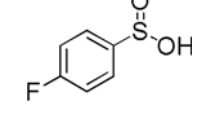
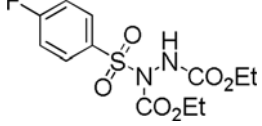
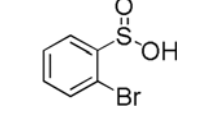
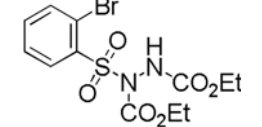
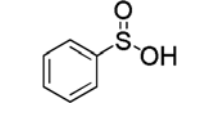
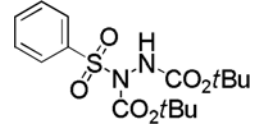
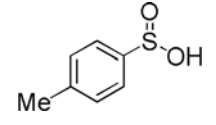
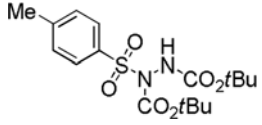
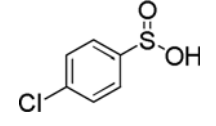
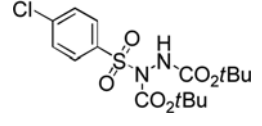
Under the optimized reaction conditions, the scope of this hydrosulfonylation reaction was investigated with a variety of sulfonic acids and azodicarboxylates, with the results shown in Table 2. In general, arylsulfonic acids which have electron-donating or electron-withdrawing groups on the aryl rings were suitable for this transformation, and the products were obtained in good to excellent yields (Table 2, entries 1–11). Various functionalities including halogen, nitro, acetyl, and acetamino groups were compatible with this reaction leading to the corresponding products **3a–3k**, which could be employed for the synthesis of more complicated derivatives via various organic transformations (Table 2, entries 4–7). In addition, naphthalene-1-sulfonic acid was also used in this reaction system to give the corresponding product **3l** in 60% yield (Table 2, entry 12). Notably, alkylsulfonic acid such

Table 2. Results for the reaction of the hydrosulfonylation of azodicarboxylates with sulfinic acids^{a,b}

Entry	Sulfinic acid	Azodicarboxylate	Product	Yield (%)
1		<i>i</i> PrO ₂ C-N=N-CO ₂ <i>i</i> Pr		3a (98%)
2		<i>i</i> PrO ₂ C-N=N-CO ₂ <i>i</i> Pr		3b (97%)
3		<i>i</i> PrO ₂ C-N=N-CO ₂ <i>i</i> Pr		3c (86%)
4		<i>i</i> PrO ₂ C-N=N-CO ₂ <i>i</i> Pr		3d (98%)
5		<i>i</i> PrO ₂ C-N=N-CO ₂ <i>i</i> Pr		3e (81%)
6		<i>i</i> PrO ₂ C-N=N-CO ₂ <i>i</i> Pr		3f (87%)
7		<i>i</i> PrO ₂ C-N=N-CO ₂ <i>i</i> Pr		3g (86%)
8		<i>i</i> PrO ₂ C-N=N-CO ₂ <i>i</i> Pr		3h (87%)
9		<i>i</i> PrO ₂ C-N=N-CO ₂ <i>i</i> Pr		3i (93%)

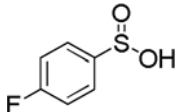
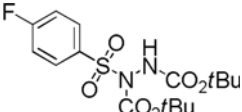
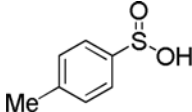
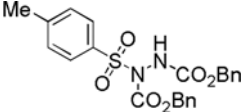
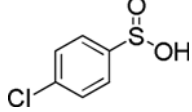
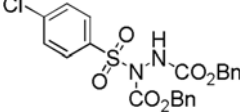
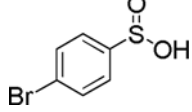
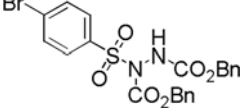
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Table 2. Continued

Entry	Sulfinic acid	Azodicarboxylate	Product	Yield (%)
10		$i\text{PrO}_2\text{C}-\text{N}=\text{N}-\text{CO}_2i\text{Pr}$		3j (88%)
11		$i\text{PrO}_2\text{C}-\text{N}=\text{N}-\text{CO}_2i\text{Pr}$		3k (97%)
12		$i\text{PrO}_2\text{C}-\text{N}=\text{N}-\text{CO}_2i\text{Pr}$		3l (60%)
13		$i\text{PrO}_2\text{C}-\text{N}=\text{N}-\text{CO}_2i\text{Pr}$		3m (87%)
14		$\text{EtO}_2\text{C}-\text{N}=\text{N}-\text{CO}_2\text{Et}$		3n (95%)
15		$\text{EtO}_2\text{C}-\text{N}=\text{N}-\text{CO}_2\text{Et}$		3o (76%)
16		$\text{EtO}_2\text{C}-\text{N}=\text{N}-\text{CO}_2\text{Et}$		3p (73%)
17		$t\text{BuO}_2\text{C}-\text{N}=\text{N}-\text{CO}_2t\text{Bu}$		3q (98%)
18		$t\text{BuO}_2\text{C}-\text{N}=\text{N}-\text{CO}_2t\text{Bu}$		3r (84%)
19		$t\text{BuO}_2\text{C}-\text{N}=\text{N}-\text{CO}_2t\text{Bu}$		3s (84%)

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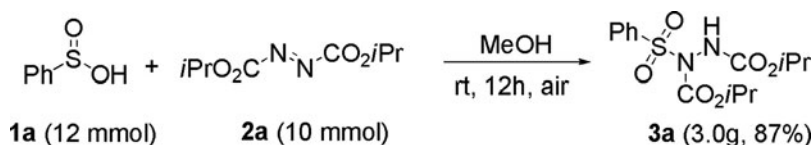
Table 2. Continued

Entry	Sulfonic acid	Azodicarboxylate	Product	Yield (%)
20		$t\text{BuO}_2\text{C}-\text{N}=\text{N}-\text{CO}_2t\text{Bu}$		3t (83%)
21		$\text{BnO}_2\text{C}-\text{N}=\text{N}-\text{CO}_2\text{Bn}$		3u (80%)
22		$\text{BnO}_2\text{C}-\text{N}=\text{N}-\text{CO}_2\text{Bn}$		3v (83%)
23		$\text{BnO}_2\text{C}-\text{N}=\text{N}-\text{CO}_2\text{Bn}$		3w (76%)

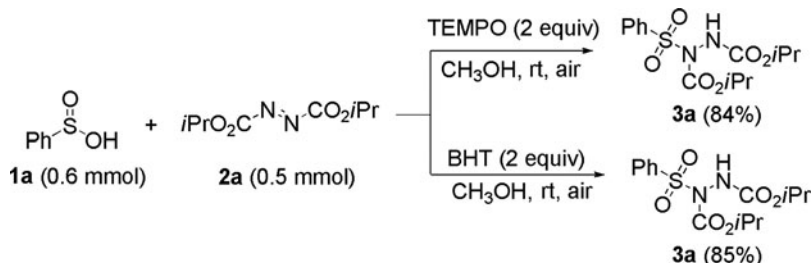
^aReaction conditions: **1** (0.6 mmol), **2** (0.5 mmol), CH_3OH (2 mL), 12–24 h, 25 °C, under air.

^bIsolated yields based on **2**.

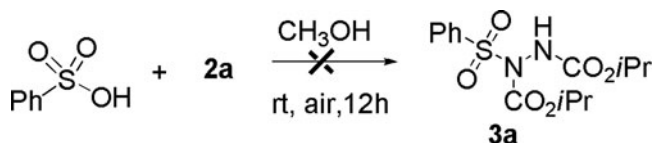
benzenesulfonic acid under the optimal conditions, no desired product was obtained (Scheme 5). Only a trace amount of product **3a** was detected when sodium benzenesulfinate was performed in the present reaction system (Scheme 6). Furthermore, the product **3a** was obtained in 95% yield when 1 equiv of CF_3COOH was added to the reaction system containing sodium benzenesulfinate and



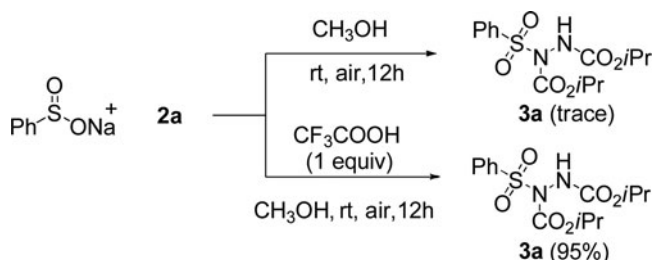
Scheme 3. Gram scale reaction.



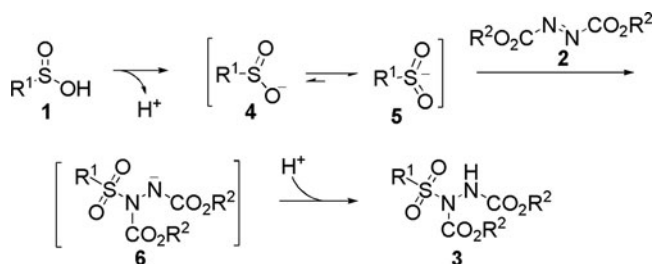
Scheme 4. Radical-capturing experiments.



Scheme 5. The reaction of benzenesulfonic acid with azodicarboxylate **2a**.



Scheme 6. The reaction of sodium benzenesulfinate with azodicarboxylate **2a**.



Scheme 7. Possible reaction pathway.

azodicarboxylate **2a** (Scheme 6). These results indicated that benzenesulfonic acid might not be an intermediate in this reaction, and the hydrogen ion played a key role in the formation of product **3a**.

Based on this information and previous reports,^[12–14] a postulated reaction pathway was proposed as shown in Scheme 7. First, sulfonic acid **2** gave the sulfinyl anion **4** resonating with more nucleophilic sulfonyl anion **5** by the loss of hydrogen proton. Subsequently, the nucleophilic addition of sulfonyl anion **5** to azodicarboxylate **2** would lead to the formation of intermediate **6**. Finally, the protonation of **6** produced the desired product **3**.

CONCLUSION

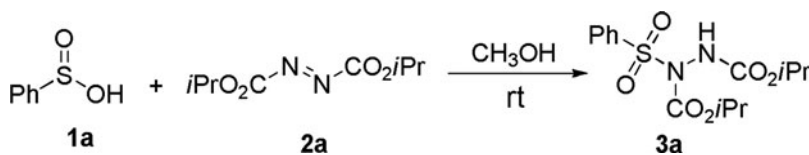
In conclusion, a novel and practical protocol of metal-free direct hydrosulfonylation of azodicarboxylates with sulfonic acids has been developed under mild conditions via direct S-N bond formation. The reaction is tolerant of a wide variety of functional groups. Taking into account the combination of desirable features, such as cheap and readily available materials, operation simplicity, high atom economy, and metal-free conditions, the proposed protocol is expected to offer a

highly efficient and attractive access to versatile sulfonylhydrazine compounds. Further applications of this new transformation in organic synthesis are underway in our group.

EXPERIMENTAL

All commercially available reagent-grade chemicals were purchased from Aldrich, Acros, Alfa Aesar, and Beijing Ouhe Chemical Company and used as received without further purification unless otherwise stated. All solvents were dried according to standard procedures. ^1H NMR and ^{13}C NMR were recorded in CDCl_3 on a Bruker Avance III 400 spectrometer with tetramethylsilane (TMS) as internal standard (400 MHz ^1H , 100 MHz ^{13}C) at room temperature, the chemical shifts (δ) were expressed in parts per million (ppm), and J values were given in hertz (Hz). The following abbreviations are used to indicate the multiplicity: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of triplets (dt), and multiplet (m). All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted were designated as multiplet (m). Mass analyses and high-resolution mass spectrometry (HRMS) were obtained on a Finnigan-LCQDECA mass spectrometer and a Bruker Daltonics Bio-TOF-Q mass spectrometer by the electrospray ionization (ESI) method, respectively. Column chromatography was performed on silica gel (200–300 mesh).

Typical Procedure for Metal-Free Direct Hydrosulfonylation of Azodicarboxylates with Sulfinic Acids



CH_3OH (2 mL) was added to a mixture of benzenesulfinic acid **1a** (0.6 mmol) and diisopropyl azodicarboxylate **2a** (0.5 mmol) in a 25-mL round-bottomed flask at room temperature. The reaction vessel was allowed to stir at room temperature for 12 h. After the reaction, the solvent was then removed under vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product **3a**.

Product 3a

Compound **3a** was obtained in 98% yield according to the typical procedure (12 h).

^1H NMR (CDCl_3 , 400 MHz, ppm): δ 8.15 (d, $J = 7.6$ Hz, 2 H), 7.65 (t, $J = 7.3$ Hz, 1 H), 7.54 (t, $J = 8.0$ Hz, 2 H), 7.17 (brs, 1 H), 5.01–4.91 (m, 2 H), 1.33–1.11

(m, 12H); ^{13}C NMR (CDCl_3 , 100 MHz, ppm): 154.6, 150.9, 138.3, 134.0, 129.4, 128.6, 73.0, 71.0, 21.9, 21.5. HRMS (ESI) calcd. for $\text{C}_{14}\text{H}_{20}\text{N}_2\text{O}_6\text{NaS}$ ($\text{M} + \text{Na}$) $^+$ 367.0940; found 367.0945.

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SUPPLEMENTAL MATERIAL

Supplemental data for this article can be accessed on the [publisher's website](#).

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